Date: 4 January 2007

Addressee: TetraTech, Inc.
                              3746 Mount Diablo Blvd.
                              Suite 300
                              Lafayette, CA 94549
                              Attn: Sujoy Roy

Submitted by: Brandi Reese, Michael Anderson and Chris Amrhein
                              University of California – Riverside

Subject: Draft Interim Report: "Hydrogen Sulfide Production and Volatilization in the Salton Sea"

We are pleased to submit this draft letter report that describes study methods and summarizes sulfide and related water column data collected from September 2005 through November 2006 in support of this project. Water column, sediment and gas phase sampling was conducted to evaluate the accumulation, volatilization and reoxidation of sulfide formed through sulfate reduction in the Salton Sea. Sulfide, sulfate, bicarbonate alkalinity, and other chemical constituents were quantified in the sediment pore water and the overlying water column, while gas phase concentrations of H_2S in the atmosphere were sampled with passive diffusion tubes.

<u>Study Methods</u>

Field

Samples were collected from three main sampling stations located in the north basin, mid-lake, and the south basin (sites 6-2, 10-2 and 14-3; Figure 1 and Table 1). The sampling program commenced in September 2005 and continued until December 2006. Field and lab measurements were made on a monthly basis from September 2005 through March 2006, on a biweekly basis from April 2006 through October 2006, and again monthly in November and December 2006. Nine additional sites along three transects (Figure 1) were sampled quarterly beginning in September 2005 until November 2006. Air samples were

collected at the pier in the southern portion of the lake (also referred to as the "Target"). Each sampling site was located using a Garmin eTrex global positioning system (GPS) and the WGS84 datum.
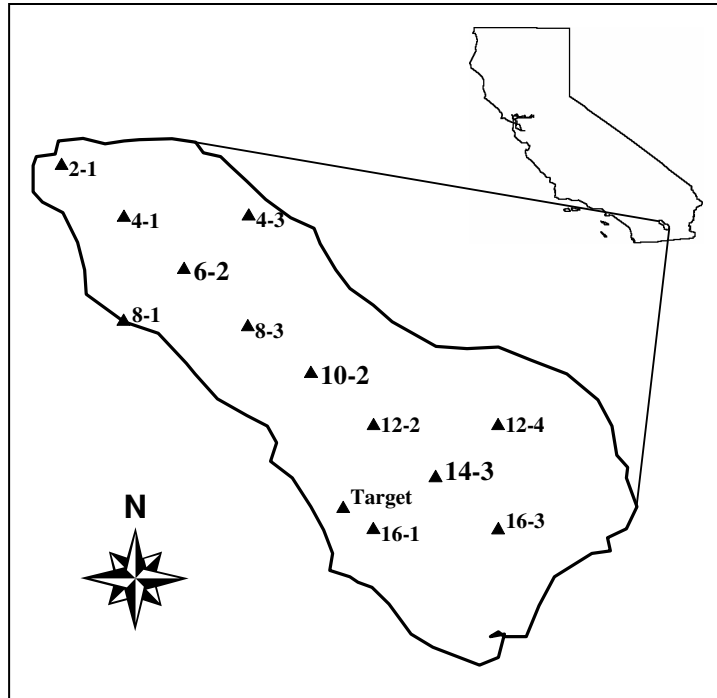

Figure 1. Locations of sampling sites

Table 1. GPS location and depth of the sampling stations.			
Site	**Mean Depth** (m)	**Latitude (degrees)**	**Longitude (degrees)**
2-1	3	33.50008	-116.0500
4-1	11.5	33.45850	-116.0000
4-3	13	33.45950	-115.9000
6-2 (North Basin)	15	33.41670	-115.9520
8-1	5.5	33.37523	-116.000
8-3	15	33.37095	-115.9005
10-2 (Mid-Lake)	12	33.33352	-115.8500
12-2	12	33.29168	-115.7998
12-4	12	33.29170	-115.7002
14-3 (South Basin)	15	33.25000	-115.750
16-1	11.5	33.20842	-115.8000
16-3	11.5	33.20833	-115.7001

Sediment

Grab samples of the upper 10 cm of sediment were collected using a Petite Ponar dredge from each site sampled. The samples were briefly homogenized and then immediately placed in 500 mL wide-mouth glass jars with a lined screw-cap lid and 250 mL Nalgene® high density polyethylene centrifuge bottles. All samples were capped with minimal headspace that was flushed with N_2 gas and stored on ice for transport to the lab.

Water Column

In situ water column measurements were made using a Hydrolab Sonde 4a calibrated following manufacturer's instructions. Hydrolab casts provided dissolved oxygen (mg/L), temperature (°C), electrical conductance (mS/cm), oxidation-reduction potential (mV), and pH as a function of depth. Measurements were made every 0.5 meter for the first 2 meters, then every meter thereafter. Transparency was also measured in the field using a 20 cm Secchi disk. Water samples were collected from the surface, mid-depth, and just above the sediment from the three main sampling sites using a 2 L Van Dorn sampler bottle. During the quarterly sampling program of the remaining nine sites, only samples of the bottom water just above the sediments were collected. Water samples were collected in triplicate for each sampling site and depth. One set of water samples was collected in 125-ml bottles, which were completely filled with water, leaving no head space. One set of water samples was acidified in the field with concentrated HNO_3 to pH<2 for total metals analysis and one set was preserved upon collection with 50% antioxidant buffer (APHA, 1998) and capped with N_2 gas for sulfide analysis. The antioxidant buffer protects the sulfide from oxidation and the high pH converts all of the H_2S_{aq} and HS^- into S^{2-}. All field samples were transported on ice to the laboratory until analysis. Analysis for H_2S was also performed in the field using a methylene blue method (APHA, 1998) with a set of pre-prepared comparators.

Atmosphere

Passive air diffusion sampling tubes were supplied by Gradko International Ltd (http://www.gradko.co.uk) and were deployed starting at 137 cm and continuing every 38 cm until a maximum of 365 cm above the surface of the water at the Target as well. Buoys were also deployed at the three main sites as well as a fourth site, 2-1, with sampling tubes located 150 cm above the surface of the water. The tube is designed to collect H_2S to an absorbent by passive diffusion. This absorbent is contained within an inert acrylic tube with a Teflon membrane and cap at one end and a mesh opening at the other end.   The tubes were sent to the manufacturer for analysis.

Laboratory Analysis

Sediment

Upon return to the lab, sediment in the glass jars was promptly analyzed for oxidation-reduction potential (ORP) and pH using a platinum electrode and a combination electrode, respectively. Subsequently, the pore water was extracted from the sediments stored in the 250 mL bottles via centrifugation (6 000-7 000 rpm, 25 min) under N_2 gas and the resulting supernatant was filtered through a 0.45-micron polycarbonate filter and promptly analyzed as described below.

Water Column and Pore Water

Unfiltered pore water and water column samples were analyzed for alkalinity by titrating to an endpoint of pH 4.5 using a Beckman Autotitrator. Concentrations of total sulfide were determined on the unfiltered pore water and the field-preserved water column samples using an Orion IonPlus silver-sulfide ion-selective electrode on a Fisher Accumet mV meter as outlined in standard methods (APHA, 1998).

For major dissolved cation (Ca^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Na^+, Si^{4+}, Sr^{2+}, K^+ and total Fe) analysis, the extracted pore water samples and water column samples were filtered with a 30 mL syringe through a 0.45-micron polycarbonate filter. The samples were then preserved by acidifying with concentrated HNO_3 to pH<2.

Due to the salinity interference, the samples were diluted 20:1 before being analyzed using the inductively coupled plasma (ICP) method on a Perkin-Elmer Optima 3000 ICP DV.

Major anions (SO_4^{2-} and Cl^-) were analyzed using filtered (described above), unacidifed pore water and water column samples, which were diluted 200:1, on a Dionex ion chromatograph with an IonPac ASII high capacity column. Dissolved Fe^{2+} was determined using the colorimetric *o*-phenanthroline method on the Milton Roy Spectronic 601 spectrophotometer at a 510 nm wavelength (APHA, 1998).

Results and Discussion

Temperature, DO and ORP

The temperature of the water column is an important parameter due to its effect on chemical and biological processes as well as oxygen solubility and thermal stratification (Stumm and Morgan, 1981). Increases in temperature typically increase the rate of chemical and biological processes and decrease oxygen solubility (Schlesinger, 1997). The vertical temperature distribution for the north basin of the Salton Sea for 2005-2006 is shown in Figure 2a. The temperature at the Sea reached a maximum of more than 32°C on 7 August 2006 in the surface waters and a minimum of 14.3°C on 2 February 2006 in the bottom waters. These findings were consistent with those of Holdren and Montaño in 1999. Temperature profiles indicate that the Sea remained relatively well mixed from the fall through the early spring, after which rapid heating began from increased solar radiation. Increased daytime heating during the spring results in the warming of the surface water, thus making the density of the surface water less than that of the cooler water below (Wetzel, 2001). If wind energy can no longer overcome this density difference, then stratification begins. Although the Salton Sea does not stably stratify for long periods of time, thermal stratification began in May 2006 when the difference in temperature of the surface to the bottom waters was more than 8°C (Figure 3a, ΔT). Stratification continued through the summer (approximately two months) until mixing occurred

in early August 2006. The temperature gradient from the surface to the bottom during the well-mixed winter months was commonly less than 1°C. The temperature profiles for the south basin and mid-lake locations showed similar seasonal heating and cooling patterns; however, the south basin appeared to have mixed more frequently as the bottom water at this site was found to be 1-3°C warmer on 2 June and 11 August indicating the warm surface water mixed to the bottom.
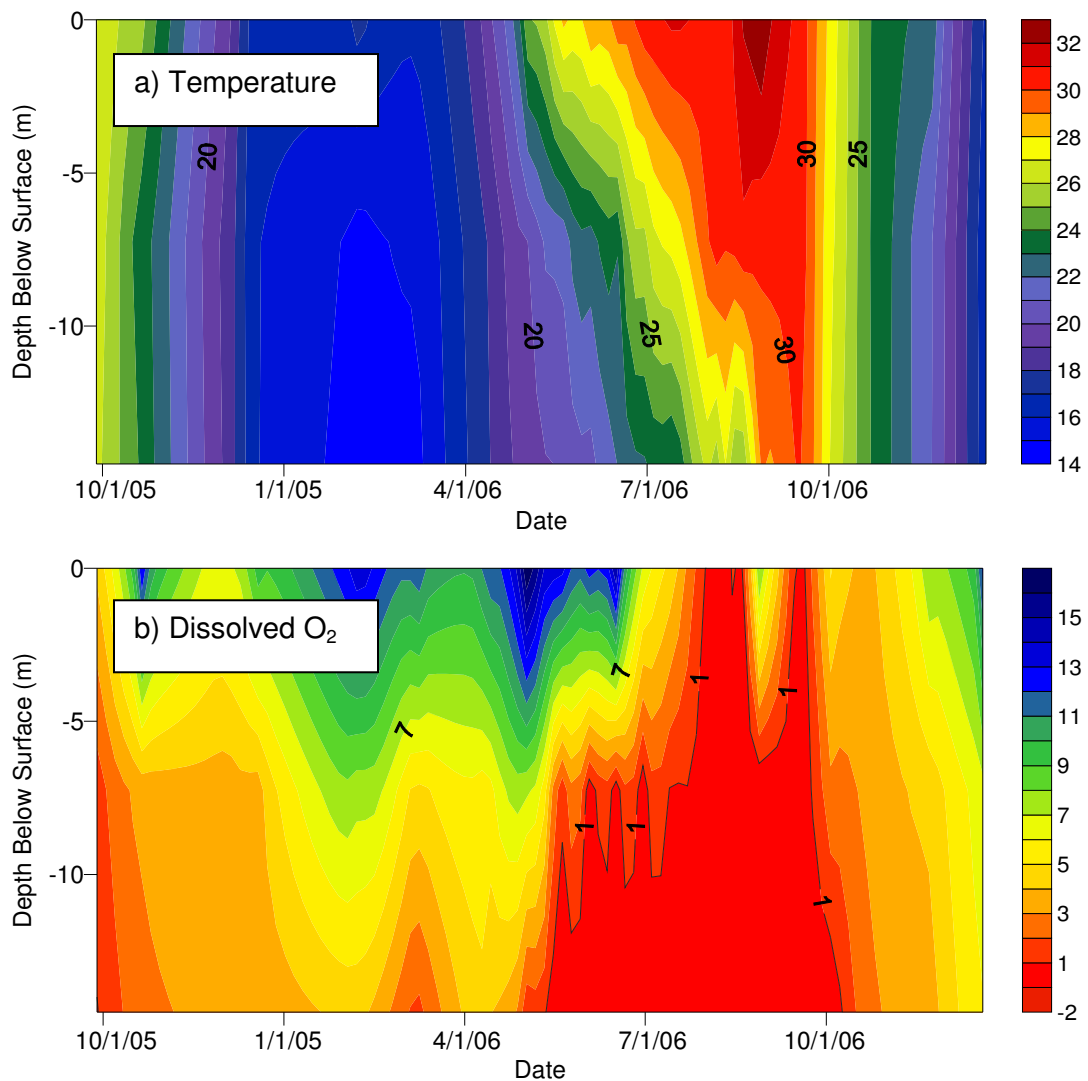

Fig. 2. Contour plots of a) temperature and b) dissolved oxygen at the north basin site (site 6-2).

The DO profiles support this assessment as well. Dissolved oxygen (DO) profiles coincided with the seasonal trends observed in the temperature profiles and are typical of a eutrophic lake system. The DO distribution for the north basin location is shown in Figure 2b. The surface waters were well aerated through the winter months and into the spring, while some oxygen depletion was observed in the bottom waters in March. The DO concentration in the epilimnion remained elevated, sometimes reaching supersturation, throughout the summer stratification period because of photosynthesis and diffusion from the atmosphere.

The hypolimnetic DO concentration declined to less than 0.5 mg/L during summer stratification because it was isolated from all sources of oxygen while organisms continued to respire and consume oxygen. Anoxic conditions can develop more easily in hypersaline environments, such as the Salton Sea, because the solubility of oxygen decreases as salinity increases (Drever, 1988). The vertical zone of anoxia spanned from approximately 7 m below the surface to the bottom sediments at a depth of about 14.5 m in the north and south basins, and to the bottom sediments (at a depth of 12 m) at the mid-lake location. The volume of the anoxic hypolimnion was often greater than 65% of the total lake volume. In contrast, Arnal (1961) noted that the bottom waters were usually oxic, with periods of anoxia developing for a few days during the summer in 1954-1956. Hypoxic or anoxic conditions in the bottom began occurring as early as late April and persisted for over two months.

During the complete mixing event in late July-early August, the zone of anoxia reached to the surface of the lake, which corresponded with a massive fish kill. Unfortunately, this trend is not uncommon at the Salton Sea and was observed by Watts et al. in 1999 (Watts et al., 2001). Reoxygenation of the water column took more than one month to complete. As expected, the oxidation-reduction potential (ORP) followed the DO concentrations, and during the period of complete anoxia was negative throughout the water column, signifying strongly reduced conditions. Unlike the water column, however, the

sediment of the Salton Sea remained anoxic and highly reduced throughout the entire year.

Hydrogen Sulfide and Related Chemistry

Sediment Porewater

Under anoxic and strongly reducing conditions (<100 mV), such as that found in the sediments of the Salton Sea, sulfate is reduced to sulfide by dissimilatory sulfate reduction (Tobolsky, 1968). We found sulfate concentrations in the Salton Sea to average around 12,0000 mg/L (125 mM). During sulfate reduction, microbes use sulfate as the terminal electron acceptor during organic matter mineralization:

$$SO_4^{2-} + 2(CH_2O) \rightarrow 2HCO_3^- + H_2S \tag{1}$$
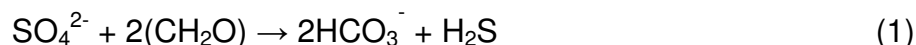
Where organic matter (CH_2O) is oxidized and bicarbonate and hydrogen sulfide are simultaneously produced. During this microbial respiration, CO_2 is produced, which reacts with carbonic acid to then dissociate to form H^+ protons (Stumm and Morgan, 1981):

$$H_2O + CO_2 \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \tag{2}$$

These reactions produce bicarbonate alkalinity (HCO_3^-) and may counteract acidification (Cook et al, 1986).

Consistent with this, we found that the sediment porewater was significantly elevated with respect to alkalinity and sulfide concentrations and lower in pH when compared to the overlying water column (Figure 3). Sulfide concentrations in the porewater increased strongly following the onset of stratification in May when the DO of the bottom water plummeted to <1 mg/L (Fig. 3). Sulfide concentrations exceeded 4 mM at site 6-2 during the summer, while the concentrations during the winter months were lower (<2 mM). Through the summer months, the mean sediment porewater concentration was greater than 3 mM in the north and south basins and 2.4 mM at the mid-lake location. During mixing in early August, a slight decrease in sulfide was observed, but recovered to an elevated level again within a couple of weeks. Overall, sulfide

concentrations in the deeper north and south basin sediments were greater than the more shallow locations.
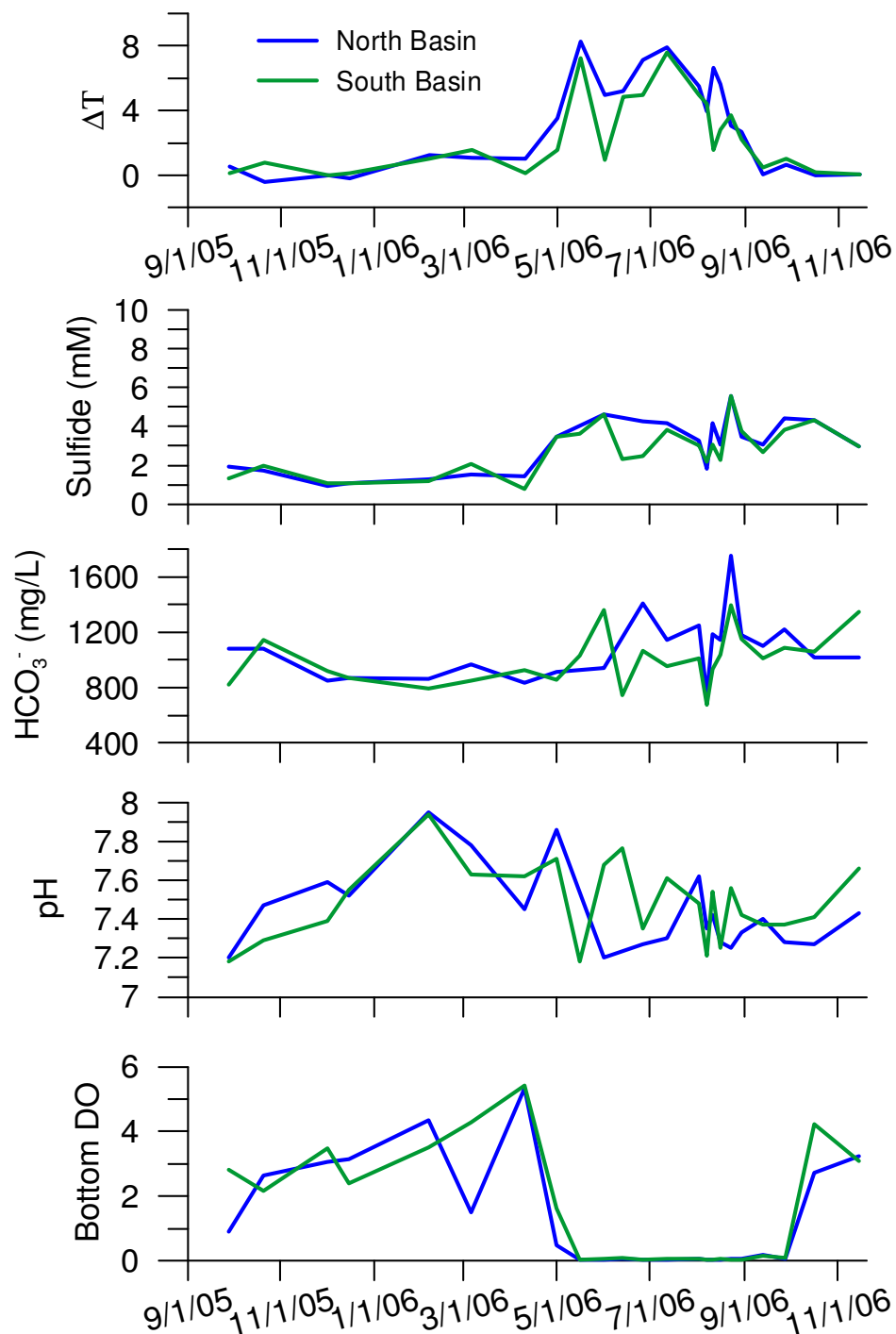

Fig. 3. Time series of sediment pore water: a) delta T, b) sulfide, c) alkalinity, d) pH and e) bottom water DO concentrations.

The pH and bicarbonate alkalinity in the sediment pore water showed smaller spatial and temporal variation (Figure 3c and 3d). The winter months had a slightly greater average pH (7.55-7.62) than did the summer-stratified months (7.43-7.52). During the mixing events, a notable decrease in the pH was also observed. The alkalinity measured was relatively stable through the winter months and slightly elevated during summer stratification. Given the increased sulfide production during summer stratification noted earlier, this trend was expected.   The deeper sites sampled quarterly in the north and south basins were higher in alkalinity, as was the northernmost site near the confluence of the Whitewater River.

In spite of low redox potential in the sediments, Fe^{2+} was not present in any significant concentration in porewater from the upper 10 cm of sediment (<0.05 mg/L). The high levels of sulfide would result in precipitation of that Fe^{2+} as insoluble iron monosulfides (FeS) and pyrite (FeS_2), thus limiting Fe^{2+} accumulation in the sediment porewater and lower water column and imparting a characteristic dark color (de Koff, et al, in review).

Bottom Water

Under aerobic conditions, like that found in the Salton Sea from late fall into early spring, sulfide was absent in the bottom waters. Once sulfide diffused out of the sediments and into the oxic water column, sulfide oxidation occurs and, assuming complete oxidation, can be represented by the following reaction:

$$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+ \tag{3}$$

The sulfide thus produced in the sediments (eq 1) is readily oxidized and consumes oxygen (i.e., is a significant source of chemical oxygen demand, COD) when transported into aerobic regions (Wetzel, 2001). The average half-life of sulfide under aerobic conditions in seawater has been determined in laboratory studies to be approximately 3-5 hours at a temperature of 24ºC and a pH of 8 (Almgren and Hagstrom, 1974).

During conditions when the Sea was well mixed and DO concentrations were elevated, no detectable (<0.004 mM) sulfide concentrations were present in

the bottom water (Fig. 4) due to the abundance of oxygen (Fig. 3e) that readily oxidized any sulfide diffusing out of the sediments. Wind stirring combined with convective mixing and limited daytime heating prevented development of thermal stratification in the late winter and early spring (Fig. 4a). Thermal stratification (as indicated by increased $\triangle$T), began in late April-early May and conincided with loss of DO (Fig. 3e) and increased sulfide in the bottom water (Fig. 4b). Development of anoxia in the bottom layer occurred almost a month later than found in the previous study of Holdren and Montano (2002), indicating the sensitivity of stratification-mixing to meteorological forcing. At this point, sulfide produced in the sediments was able to diffuse into an increasingly anaerobic bottom layer and begin to accumulate substantially in the hypolimnion.

After a little more than two months of limited mixing and accumulation of sulfide, concentrations reached the highest levels in late July in the north basin (Figure 4) (0.94 mM). These concentrations appear to be quite high based on the relatively short length of time sulfide accumulated. For example, Mono Lake, a much deeper (48 m) hypersaline lake with a smaller fetch, has been subject to prolonged periods of stratification and presumably greater sulfide accumulation. Miller, et al reported sulfide concentrations that reached 1.82 mM in the mixolimnion of Mono Lake during a 4-year period of meromixis from 1984 to 1988, only twice that of the Salton Sea during three months of stratification. Walker Lake in Nevada, also a deeper (29 m) saline lake with smaller surface area subject to wind mixing, had reported concentrations of only 0.3 mM in the hypolimnion following a 6 to 7 month stratification period (Beutel et al, 2001).

Sulfide concentrations in the bottom waters appear to be increasing at the Sea over the past five decades. In 1955, sulfide at the Sea was measured to be maximally 0.003 mM during the summer, in which stratification lasted only a few days (Carpelan, 1958). In 1998-1999, sulfide concentrations were reported to be 0.09 - 0.2 mM in the bottom (Watts et al, 2001), following a longer period of stratification and hypolimnetic anoxia than found in this study. The increases in sulfide at the Salton Sea could be a result of greater sulfate concentrations or an

increase in organic matter and thus more sulfate reduction; more likely it is the combination of the two.
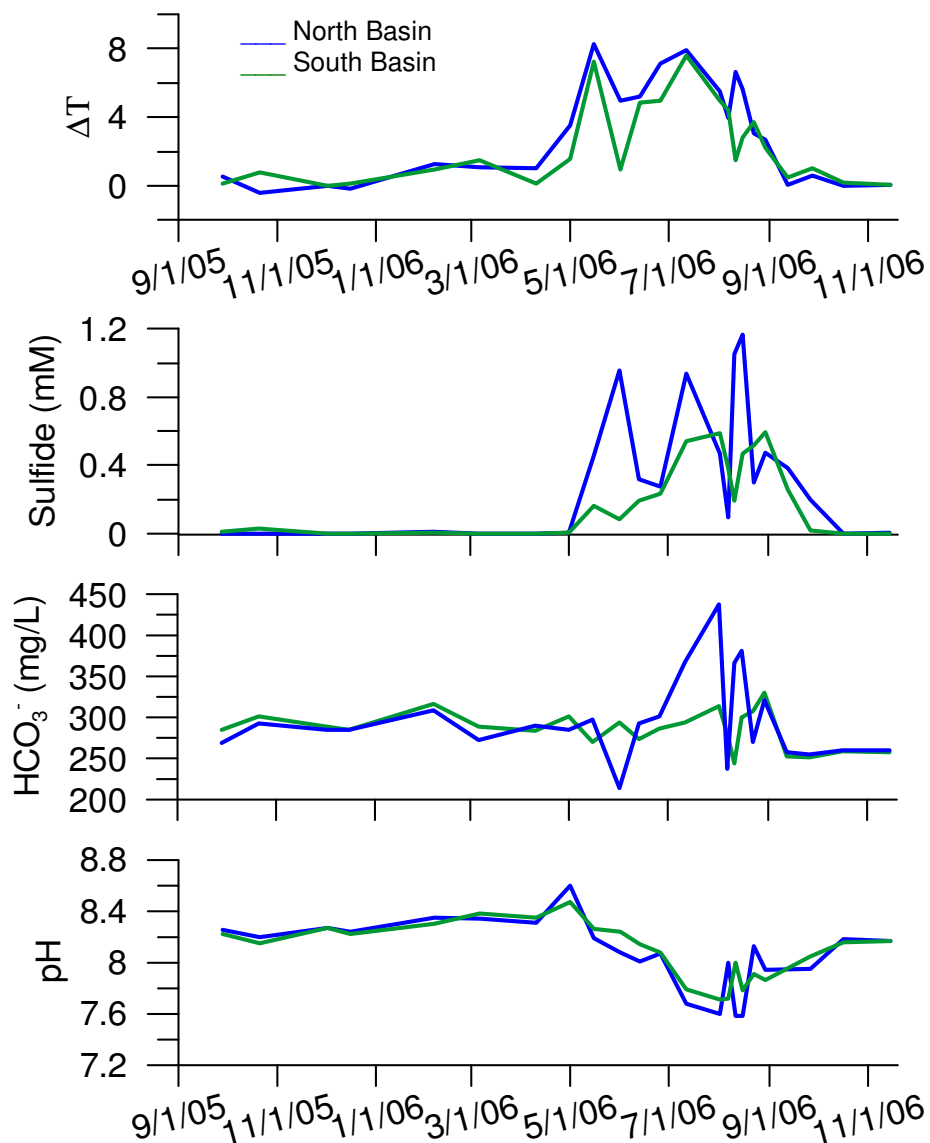

Fig. 4. Time series of bottom (hypolimnetic) water concentrations: a) delta T, b) sulfide, c) alkalinity, and d) pH.

The concentrations of sulfide in the south basin were lower than that of the north basin, while the mid-lake location consistently had the lowest sulfide concentrations overall (data not shown). This mid-lake site, as noted earlier, is shallower than the north and south basins and had a thicker oxic stratum, which

provided for less build-up of sulfide concentration in the bottom layer. Sampling locations closer to shore also had lower sulfide concentrations. Watts et al. (2001) hypothesized that the shallower locations are subject to convection driven by greater nocturnal cooling of shallow waters, which probably contributes to the greater oxygenation and mixing of the near-shore (and shallower) waters.

The same trend in bottom water pH and bicarbonate alkalinity (Fig. 4c,d) was present as that found for the sediment pore water (Fig. 3c,d). Alkalinity was relatively constant at 275 mg HCO_3^-/L through the winter and increased somewhat during summer stratification. The pH was also relatively stable (average 8.25-8.35) through the (well-mixed) winter months, but during stratification, the pH dropped to its minimum in late July to 7.6 and 7.7 in the north and south basins, respectively. In this pH range, sulfide is approximately 90% is HS^-, approximately 10% is the more toxic form of H_2S, and less than 0.1% is as S^{2-} (Stumm and Morgan, 1981; Wetzel, 2001).

When dissolved oxygen is the limiting reagent, such as the case of summer stratification, sulfide can quickly consume all of the available oxygen (Cline and Richards, 1969). Most minor mixing events resulted in the oxidation of upwelled hypolimnetic H_2S in the epilimnion, however, this was not the case during the mixing in August. During the August 2006 mixing, sulfide in the bottom decreased as the water mixed upward depleting the surface waters of available oxygen. Simultaneously, aerated surface water mixed downward to dilute the sulfide-rich bottom waters, providing some oxygen for sulfide oxidation to occur in the lower water column. The alkalinity concentration initially increased then decreased during mixing, perhaps indicating greater sulfate reduction taking place initially followed by sulfide oxidation (Fig. 4).

The trend in pH was consistent with the observations in sulfide and alkalinity during mixing. Experimental data suggests that pH decreases 0.1–0.2 log units in which the oxidation of the weak acid HS- reduces the pH and alkalinity through the formation of stronger sulfoxy acids (Cline and Richards, 1969). The pH during mixing averaged 8.12 - 8.18 and was relatively uniform from the surface into the bottom layer.

Surface Water

The uppermost meter or so of the water column has greater exchange with the atmosphere, potentially higher rates of photosynthesis, and as such, greater DO concentrations. The Sea experiences strong, frequent winds events from the fall to the spring that allow for turbulent mixing. This was observed not only in our study, but also by Carpelan (1955), Arnal (1961), Watts, et al (2001), and Holdren and Montaño (2002). The well-mixed and well-aerated conditions in the surface waters during the winter months suppressed any sulfide accumulation, and sulfide was largely undetected (with the exception of measurements made on 2 December 2006, in which sulfide in the north basin was 0.01 mM) (Figure 5a). This may have coincided with late season, transient stratification followed by a local mixing event prior to sampling.

Even as thermal stratification began in late spring, the upper few meters of the water column continued to mix and, as noted earlier, contained high levels of DO, and any sulfide in the water column was mostly reoxidized by mid-depth. On 1 June 2006, however, the sulfide concentration in the north basin at 7 m reached 0.2 mM although the south basin contained much lower sulfide concentrations (0.01 mM). The lower concentrations observed in the south basin were perhaps due to more frequent mixing (Watts et al, 2001).

After a few months of stratification (interrupted with periodic mixing by upwelling and convective mixing), sulfide was consistently being observed at mid-depth as well as in the hypolimnion (data not shown). During more complete mixing that occurred in late July-early August, sulfide from the lower water column (e.g., the bottom and middle sampling depths) mixed up to the surface layer of the water column, depleting the entire water column of DO. On 2 August 2006, sulfide was measured in the surface water at 0.1 mM in the north basin, 0.02 mM in the south basin, and 0.01 mM at the mid-lake location. Sulfide concentrations in the surface waters remained elevated and the water remained anoxic for over two weeks following mixing.
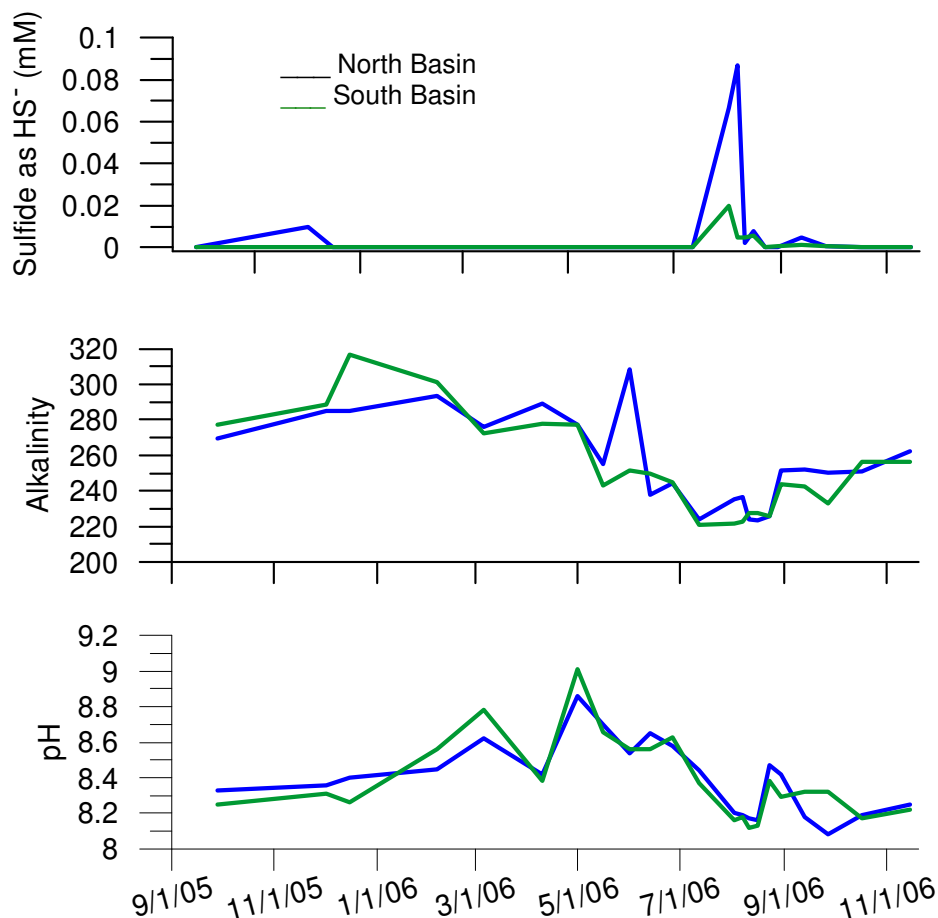
Fig. 5. Time series of surface (approximately 1 m depth) concentrations of a) sulfide, b) alkalinity and c) pH.

Atmosphere

The concentration of H_2S in the air approximately 1-2 m above the surface of the Salton Sea at the target was consistently elevated compared to that of the background location approximately 6.5 kilometers north of the lake. The concentration of the hydrogen sulfide in the air phase averaged about 1 $\mu g/m^3$ through the winter and spring, although the concentration exceeded 30 $\mu g/m^3$ in July-August (Fig. 6), coinciding with the mixing event that increased sulfide levels throughout the water column (Fig. 5a). Volatilization is thus a potentially important loss process for H_2S following mixing.
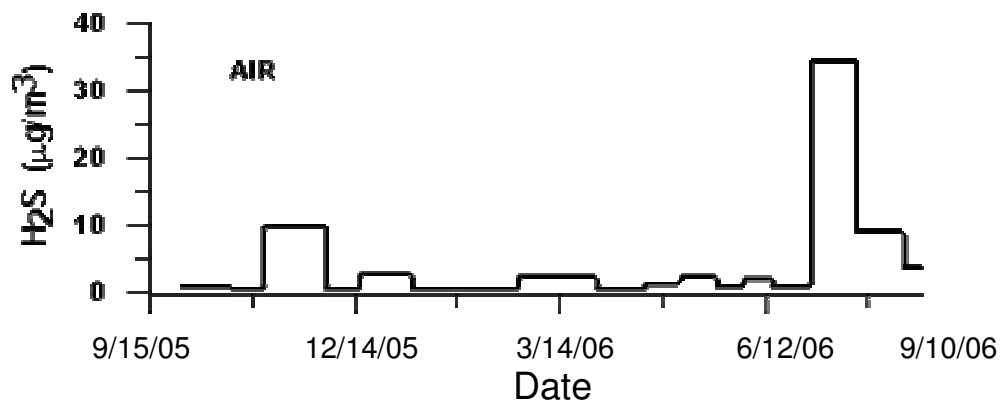
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Fig. 6. Atmospheric H₂S concentration at the "target".

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